

Representing Vapor–Liquid Equilibrium for an Aqueous MEA–CO₂ System Using the Electrolyte Nonrandom-Two-Liquid Model

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Following the work of Austgen et al., the electrolyte nonrandom-two-liquid (NRTL) model was applied in a thermodynamically consistent manner to represent the vapor–liquid equilibrium (VLE) of the aqueous monoethanolamine (MEA)–CO₂ system with rigorous chemical equilibrium consideration. Special attention was given to the accurate VLE description of the system at both absorbing and stripping conditions relevant to most aqueous MEA absorption/stripping processes for CO₂ removal. The influence from chemical equilibrium constants, Henry's constant, experimental data, and data regression on the representation of the VLE of the system was discussed in detail. The equilibrium constant of the carbamate reversion reaction as well as important interaction parameters of the electrolyte NRTL model were carefully fitted to experimental data. A good agreement between the calculated values and the experimental data was achieved. Moreover, the model with newly fitted parameters was successfully applied to simulate three industrial cases for CO₂ removal using a rate-based approach. The results from this work were compared with those using the model by Austgen et al.

Introduction

Aqueous monoethanolamine (MEA) is widely used for the removal of CO₂ from gas streams. It has several advantages over other commercial alkanolamines:

(a) It is the strongest base with the quickest reaction rate, yielding the highest purity, which make it most suitable for processing to-be-liquefied natural gas, synthesis gas, and hydrogen stream, which require low CO₂ leakage.

(b) It has the lowest molecular weight and thus the highest absorbing capacity on a weight basis. Furthermore, its cost is low.

(c) It is very thermally stable and less likely to undergo thermal degradation.

(d) It has a relatively low solubility for hydrocarbon which reduces the hydrocarbon loss when processing the natural gas and refinery gas streams.

The disadvantages of aqueous MEA include the following:

(a) It has a high reaction heat with CO₂ that leads to higher stripping energy consumption.

(b) It is unable to remove mercaptans.

(c) It forms degradation products with COS, CS₂, and oxygen-bearing gases.

(d) It suffers more vaporization loss than other alkanolamines because of its higher vapor pressure.

(e) It is appreciably more corrosive than many other alkanolamines.

In 1990, aqueous MEA comprised 40% of the market (Dupart et al.²). Although its market share has decreased in recent years, it remains as one of the principal acid gas absorbents with significant commercial importance. There are still strong commercial interests in minimizing equipment and operation costs for aqueous MEA absorption/stripping processes for CO₂ removal. Computer process simulation is an effective means for optimizing the design and operation of the

CO₂ removal process and for achieving a business competitiveness.

A thermodynamic property model capable of accurate representation of the vapor–liquid equilibrium (VLE) of the aqueous MEA–CO₂ system is essential for a successful computer simulation of the process. In the last few decades, considerable progress has been made in modeling VLE of the acid gas (CO₂ and H₂S) in aqueous alkanolamine systems, including the aqueous MEA–CO₂ system.

A practical and widely used model was proposed by Kent and Eisenberg.³ This model is essentially the Klyamer–Kolesnikova–Rodin model,⁴ assuming all activity coefficients and fugacity coefficients as unity (ideal liquid and vapor phases). The chemical reaction equilibria are defined in the liquid phase. The equilibrium constants of the amine dissociation reaction and carbamate formation reaction are regressed based on the experimental acid gas solubility data in the aqueous amine systems. The Kent–Eisenberg model has some deficiencies: the fit is good only in a limited loading range, and its extension to the mixed acid gas is less successful. However, the model has been popular among practitioners because it correlates the experimental data reasonably well while retaining extreme computational simplicity.

A more rigorous and therefore more generally applicable model was proposed by Deshmukh and Mather.⁵ It uses the same chemical reactions in the liquid phase as the Kent–Eisenberg model does, but instead of assuming activity coefficients to be unity, these activity coefficients, except for water, are calculated by an extended expression of the Debye–Hückel theory proposed by Guggenheim and Stokes.⁶ The activity coefficient of water is still set as unity. The interaction parameters in the Guggenheim–Stokes expression were obtained from regression of experimental VLE data. Weiland and co-workers⁷ provided the values of the Guggenheim–Stokes interaction parameters for most of the commercially important amine systems over a

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wide range of conditions. Later, a similar model was proposed by Li and Mather.⁸ The Guggenheim–Stokes expression was replaced by the well-known Pitzer model to calculate the activity coefficients. The Pitzer interaction parameters were determined from experimental data for the MEA–CO₂–H₂O and methyldiethanolamine (MDEA)–CO₂–H₂O systems. On the basis of these parameters, good VLE prediction for the MEA–MDEA–CO₂–H₂O system was achieved.

Probably the most sophisticated and thermodynamically rigorous model available at this time was proposed by Austgen et al.¹ This model was based on the electrolyte nonrandom-two-liquid (NRTL) model of Chen and co-workers.^{9,10} Not only water but also alkanolamines were regarded as solvents. So, the solution was treated as a mixed-solvent system. The model accounted for the rigorous chemical equilibria and mass balance and thus provided the insight of various ionic and molecular species in the liquid phase. The activity coefficients in the liquid phase were represented with the electrolyte NRTL model treating both long-range ion–ion interactions and short-range interactions between all true species in the liquid phase. The fugacity coefficients in the vapor phase were represented using the Redlich–Kwong equation of state modified by Soave.¹¹ Under the absorber column condition of the alkanolamine–CO₂ removal process, the vapor fugacity coefficients should not be neglected. The model is particularly suitable for the column simulation based on the kinetics and mass- and heat-transfer rates because it provides vital information such as interface VLE, bulk interface driving forces, and true liquid species. The model by Austgen et al.¹ has been used to simulate the aqueous MEA absorption/stripping processes for CO₂ removal using the rate-based approach. The simulation result of the absorber column was good. However, the result of the stripper column was not satisfactory; especially the reboiler duty was overpredicted. Further improvement is, therefore, necessary.

The objective of this work is to investigate the cause which makes the model by Austgen et al.¹ predict a high reboiler heat duty of the stripper column and to improve the model so it is capable of accurately describing the VLE of the system at both absorbing and stripping conditions relevant to the common aqueous MEA absorption/stripping processes for CO₂ removal.

Electrolyte NRTL Model

The electrolyte NRTL model used by Austgen and co-workers¹ and in this work consists of three contributions. The first contribution is the long-range contribution represented by the Pitzer–Debye–Hückel expression, which accounts for the contribution due to the electrostatic forces among all ions. The second contribution is an ion-reference-state-transfer contribution represented by the Born expression. In the electrolyte NRTL model, the reference state for ionic species is always infinitely dilute state in water even when there are mixed solvents. The Born expression accounts for the change of the Gibbs energy associated with moving ionic species from a mixed-solvent infinitely dilute state to an aqueous infinitely dilute state. The Born expression drops out if water is the sole solvent in the electrolyte system. The third contribution is a short-range contribution represented by the local-composition electrolyte NRTL expression, which accounts for the contribution due to short-range interac-

tion forces among all species. The electrolyte NRTL expression was developed based on the NRTL local-composition concept (Renon and Prausnitz¹²), the like-ion repulsion assumption, and the local electroneutrality assumption. The like-ion repulsion assumption stipulates that in the first coordination shell of a cation (anion) the local composition of all other cations (anions) is zero. The local electroneutrality assumption imposes a condition that in the first coordination shell of a molecular species the composition of cations and anions is such that the local electric charge is zero.

The Pitzer–Debye–Hückel expression for excess Gibbs energy, normalized to a mole fraction of unity for the solvent and zero mole fraction for ions, is given as follows:

$$\frac{g^{\text{ex},\text{PDH}}}{RT} = -\left(\sum_k x_k\right) \left(\frac{1000}{M_s}\right)^{1/2} \left(\frac{4A_\Phi I_x}{\rho}\right) \ln(1 + \rho I_x^{1/2}) \quad (1)$$

where

$$A_\Phi = \left(\frac{1}{3}\right) \left(\frac{2\pi N_0 d}{1000}\right)^{1/2} \left(\frac{e^2}{DkT}\right)^{2/3}$$

$$I_x = \frac{1}{2} \sum_i Z_i^2 x_i$$

The Born expression for excess Gibbs energy is given as follows:

$$\frac{g^{\text{ex},\text{Born}}}{RT} = \frac{e^2}{2kT} \left(\frac{1}{D} - \frac{1}{D_w}\right)^{1/2} \left(\sum_i \frac{x_i Z_i^2}{r_i}\right) \times 10^{-2} \quad (2)$$

where D stands for the dielectric constant of the solvent mixture with the same solvent ratio as that in the electrolyte solution. D_w is the dielectric constant of water.

The local-composition electrolyte NRTL expression for excess Gibbs energy is given as follows:

$$\frac{g^{\text{ex},\text{lc}}}{RT} = \sum_m X_m \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} +$$

$$\sum_c X_c \sum_{a'} \left(\frac{X_{a'}}{\sum_{a''} X_{a''}} \right) \frac{\sum_j X_j G_{jc,a'a'} \tau_{jc,a'a'}}{\sum_k X_k G_{kc,a'a'}} +$$

$$\sum_a X_a \sum_{c'} \left(\frac{X_{c'}}{\sum_{c''} X_{c''}} \right) \frac{\sum_j X_j G_{ja,c'a} \tau_{ja,c'a}}{\sum_k X_k G_{ka,c'a}} \quad (3)$$

where

$$\begin{aligned}
G_{jm} &= \exp(-\alpha_{jm}\tau_{jm}) \\
G_{jc,ac} &= \exp(-\alpha_{jc,ac}\tau_{jc,ac}) \\
G_{ja,ca} &= \exp(-\alpha_{ja,ca}\tau_{ja,ca}) \\
G_{cm} &= \frac{\sum_a X_a G_{ca,m}}{\sum_{a'} X_{a'}} \\
G_{am} &= \frac{\sum_c X_c G_{ca,m}}{\sum_{c'} X_{c'}} \\
\alpha_{cm} &= \frac{\sum_a X_a \alpha_{ca,m}}{\sum_{a'} X_{a'}} \\
\alpha_{am} &= \frac{\sum_c X_c \alpha_{ca,m}}{\sum_{c'} X_{c'}} \\
\tau_{mc,ac} &= \tau_{cm} - \tau_{ca,m} + \tau_{m,ca} \\
\tau_{ma,ca} &= \tau_{am} - \tau_{ca,m} + \tau_{m,ca}
\end{aligned}$$

The variables τ_{cm} and τ_{am} are computed accordingly from G_{cm} and G_{am} . It is worth mentioning that the first term on the right-hand side of eq 3 represents the short-range interaction contribution where the molecular species are the local center and the second and third terms account for the short-range interaction contributions where cations and anions are the local center, respectively.

After proper consideration of unsymmetrical convention for the solutes and ionic species, the complete excess Gibbs energy expression of the electrolyte NRTL model is given as follows:

$$g^{\text{ex}*} = g^{\text{ex},\text{PDH}} + g^{\text{ex},\text{Born}} + g^{\text{ex},\text{lc}} \quad (4)$$

The activity coefficient for any species i , ionic or molecular, solute or solvent, is derived from the partial derivative of the excess Gibbs energy with respect to the mole number of species i :

$$\ln \gamma_i = \frac{1}{RT} \left[\frac{\partial(n_t g^{\text{ex}*})}{\partial n_i} \right]_{T,P,n_{j \neq i}} \quad (5)$$

where n_t is the total mole number for all species in the system.

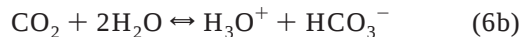
Basic Solution Chemistry

MEA is a primary amine that has two hydrogen atoms directly attached to a nitrogen atom. Following the work of Austgen and co-workers,¹ the principal reactions occurring in the aqueous MEA-CO₂ system are written as

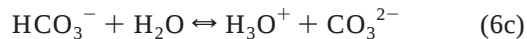
Ionization of water



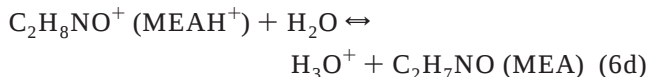
Hydrolysis and ionization of dissolved CO₂



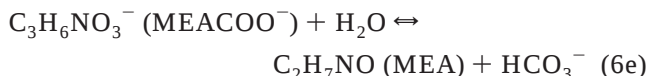
Dissociation of bicarbonate



Dissociation of MEAH⁺ (protonated MEA)



MEACOO⁻ (carbamate) reversion to bicarbonate



Additional reactions other than the above ones may occur to produce nonregenerable heterocyclic compounds (Kohl and Nielsen¹³). We chose not to include these degradation reactions because they are not considered important in the basic aqueous MEA absorption/stripping operation for CO₂ removal. MEA may also react with COS, CS₂, and oxygen-bearing gases to form degradation products. These reactions were not taken into account in this work.

Problem Analysis and Resolution

The model by Austgen et al.¹ has been used to simulate the aqueous MEA absorption/stripping processes for CO₂ removal using the rate-based approach. The simulation result of the absorber column was good. However, the result of the stripper column was not satisfactory; especially the predicted reboiler heat duty was too large. The first objective of this work is to investigate the cause that makes the model predict a high reboiler heat duty of the stripper. In an initial study, we carefully analyzed the heat consumed in the stripper column.

In a conventional stripping operation, heat is supplied to the column by steam or by other heat mediums within tubes in the reboiler. The heat is consumed mainly for three purposes: (1) to raise the temperature of the rich solution feeding the column to the temperature of the lean solution leaving the reboiler, (2) to reverse the MEA-CO₂ reactions and dissociate the MEA-CO₂ compounds, and (3) to vaporize water into steam which serves as the stripping vapor. We separated the amount of heat consumed for each purpose based on the simulation result in the stripper condition using the model by Austgen et al.¹ We found that the quantities of heat consumed for the first two purposes were reasonable. However, the heat consumed for the third purpose was too high because too much water was being vaporized. This indicates that the model does not accurately describe the VLE under the stripper condition. As pointed out by Kohl and Nielsen,¹³ the inability to make an accurate VLE description for the stripper column is a common problem for many models proposed for designing and simulating the amine acid-gas processes. Although the following analysis is aimed at the model by Austgen et al.,¹ it might be beneficial to other models as well.

Now we can rephrase the objective of this work more precisely as improving the VLE representation for the MEA-CO₂-H₂O system in the stripper condition using the model by Austgen et al.¹ In the work by Austgen et al., both water and MEA are regarded as solvents. So, the MEA-CO₂-H₂O system was treated as a mixed-solvent electrolyte system. The vapor-liquid equilibria for the solvent species are given by

$$y_s \phi_s^v P = x_s \gamma_s \phi_s^0 P_s^0 \exp\left(\frac{v_s(P - P_s^0)}{RT}\right) \quad (7)$$

The vapor-liquid equilibria for the supercritical components are given by

$$y_i \phi_i^v P = x_i \gamma_i \left(\frac{H_i^m}{\gamma_i^\infty}\right) \exp\left(\frac{\bar{v}_{i-m}^\infty(P - P_m^0)}{RT}\right) \quad (8)$$

where

$$\ln\left(\frac{H_i^m}{\gamma_i^\infty}\right) = \sum_s w_s \ln\left(\frac{H_{i-s}}{\gamma_{i-s}^\infty}\right) \quad (8a)$$

H_{i-s} is Henry's constant for solute i , in the pure solvent s , at the system temperature and saturation pressure of the solvent s ; γ_{i-s}^∞ is the infinite dilution activity coefficient for solute i , in the pure solvent s , at the system temperature; w_s is the weight fraction for the solvent s , based on the true solvent composition ratio in the MEA-CO₂-H₂O system; v_s is the molar volume of the pure solvent at the system temperature and saturation pressure P_s^0 ; $\bar{v}_{i-m}^\infty$ is the partial molar volume for solute i , at infinite dilution in the solvent mixture at the system temperature and saturation pressure of the solvent mixture P_m^0 ; x is the true mole fraction in the liquid phase which is based on all species, molecular and ionic, after consideration of solution chemistry.

It should be noted that, in the work by Austgen et al., a simplification was made that Henry's constants in pure MEA are replaced by those in pure water. The Poynting correction of eq 8, i.e., the exponential term, was changed accordingly.

After closely examining the vapor-liquid equilibria of the MEA-CO₂-H₂O system at the stripper condition combining the all-around analysis of eqs 7 and 8, we decided to pursue the improvement by considering (1) equilibrium constants for the reactions in the liquid phase, (2) Henry's constant of CO₂ in the MEA-H₂O solvent mixture, (3) evaluation of experimental data, and (4) equilibrium constant and interaction parameters from data regression.

It is worth mentioning that, because the pressure of the stripper column is low, the Poynting correction in eqs 7 and 8 is not a key influential factor on VLE of the system under the stripper condition.

Equilibrium Constants for the Reactions in the Liquid Phase. Equilibrium constants govern the extent of reactions 6a-e and determine the true composition in the liquid phase, thereby greatly influencing the VLE of the MEA-CO₂-H₂O system.

The equilibrium constants of reactions 6a-e in the model by Austgen et al.¹ were carefully examined. We found that the equilibrium constants used by Austgen et al. for reactions 6a (ionization of water), 6b (hydroly-

sis and ionization of dissolved CO₂), and 6c (dissociation of bicarbonate) are well-grounded because these equilibrium constants were fitted based on extensive experimental data and had been used successfully in VLE representation of many other aqueous electrolyte systems containing CO₂. We continue using these equilibrium constants without change.

For reaction 6d (dissociation of protonated MEA), Austgen and co-workers obtained the equilibrium constant based on the experimental data of Bates and Pinching.¹⁴ The temperature range of the Bates-Pinching data is only from 0 to 50 °C. The common temperature range in the stripper column is around 120 °C. The temperature extrapolation might cause improper dissociation of protonated MEA at the stripper column which ultimately affects the accuracy of VLE calculation. To ascertain whether the temperature extrapolation by Austgen et al. is proper, we perturbed the equilibrium constant at the stripper condition around the extrapolation value of Austgen et al. and used the perturbed value for the simulation of three industrial cases. The simulation results suggested that the temperature extrapolation by Austgen et al. was in the reasonable range. Because the equilibrium constant at the stripper condition is still unknown, we accepted the temperature extrapolation by Austgen et al. However, we point out that there are many uncertain factors impeding the accurate VLE description for the MEA-CO₂-H₂O system. It would be well worth the effort to eliminate this uncertainty by directly measuring the equilibrium constant at the stripper condition.

As for reaction 6e (carbamate reversion to bicarbonate), one section in the paper by Austgen and co-workers¹ has been specifically dedicated to the discussion of the reaction. The discussion basically states that the experimental equilibrium constant reported in the literature was very limited for the carbamate reaction. Furthermore, the quality of the literature data was not well justified for the direct use. Therefore, Austgen and co-workers chose to treat the carbamate equilibrium constant as an adjustable parameter. It was fitted, simultaneously with the appropriate interaction parameters of the electrolyte NRTL model, on the VLE data of the MEA-CO₂-H₂O system. On the basis of our experiences, the simultaneous fit of both the equilibrium constant and the interaction parameters might result in overfitting of the data. It has been noticed that the VLE measurement for the MEA-CO₂-H₂O system may have errors up to and even beyond 40% (detail can be seen in the subsequent section entitled Evaluation of Experimental Data). Overfitting of these data is likely to have a negative effect on the actual process simulation calculation. Weiland and co-workers⁷ proposed a two-stage procedure for fitting the VLE data for the alkanolamine (including MEA)-CO₂-H₂O systems. First, the equilibrium constants were fitted based on the VLE data. Second, based on the same VLE data, the interaction parameters were adjusted to achieve the best possible results. In this work, we adopted the two-stage procedure by Weiland et al. Therefore, the equilibrium constant for reaction 6e was obtained from the first-stage fitting.

In the model by Austgen et al.¹ and in this work, the temperature function of equilibrium constants for reac-

Table 1. Temperature Dependence of the Equilibrium Constants for Reactions 6a–e

$$\ln K = C_1^k + C_2^k/T + C_3^k \ln T + C_4^k T$$

reaction	C_1^k	C_2^k	C_3^k	C_4^k	ref
6a	132.899	-13445.9	-22.4773	0.0	<i>a</i>
6b	231.465	-12092.1	-36.7816	0.0	<i>a</i>
6c	216.049	-12431.7	-35.4819	0.0	<i>a</i>
6d	0.79960	-8094.81	0.0	-0.007484	<i>b</i>
6e	1.282562	-3456.179	0.0	0.0	<i>c</i>

^a Austgen et al.¹ ^b Austgen et al.,¹ with MEA infinitely dilute activity coefficient correction. ^c Fitted on the VLE data.

tion 6a–e is represented as

$$\ln K = C_1^k + \frac{C_2^k}{T} + C_3^k \ln T + C_4^k T \quad (9)$$

K is the equilibrium constant which is dimensionless. Coefficients, C_1^k – C_4^k , used in this work are summarized in Table 1 for reactions 6a–e. Note that the coefficients of reaction 6d are somewhat different from those in the model by Austgen et al.¹ That is because in this work the MEA–H₂O interaction parameter values have been changed, which produce the different values of the infinitely dilute activity coefficient for MEA in water, and the coefficients of reaction 6d in Table 1 reflect this change accordingly.

Henry's Constant of CO₂ in the MEA–H₂O Solvent Mixture. Henry's constant of CO₂ has a direct effect on the VLE of the MEA–CO₂–H₂O system. In the model by Austgen et al.,¹ both H₂O and MEA are treated as solvents. According to eq 8a, we need to know Henry's constants of CO₂ in the two pure solvents: water and MEA. Henry's constant of CO₂ in H₂O used by Austgen et al. is well-established and well-tested. Therefore, it was kept in this work without modification. Because of the chemical reactions, Henry's constant of CO₂ in MEA cannot be directly measured. Austgen and co-workers assumed that its value would be the same as that in water. The assumption simplified the calculation. However, it might introduce errors in the final simulation. Because the available experimental VLE data of the MEA–CO₂–H₂O system are the CO₂ solubility data, adjustable parameters are fitted according to eq 8 only. The electrolyte NRTL model for activity coefficient is a thermodynamically rigorous model and satisfies the Gibbs–Duhem relationship. Thus, the activity coefficients for the solvents, i.e., water and MEA, in eq 7 are calculated using the fitted parameters based on eq 8. When Henry's constant for CO₂ in pure MEA is assumed as that in water, it will influence the fitted parameter values according to eq 8. Consequently, it will affect the activity coefficient of water and MEA, which as a result changes the partial vapor pressure of water and MEA. Evidently, the effect increases when the MEA concentration increases. Also, when the CO₂ loading decreases, more MEA stays in molecular form and the assumption becomes less suitable. In the stripper column, the partial vapor pressure of water becomes significant and the assumption might cause significant errors.

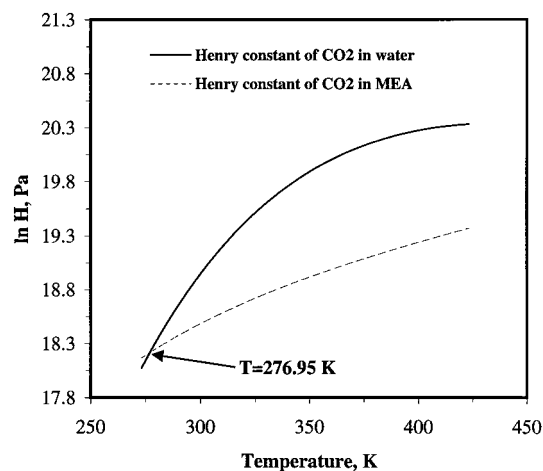
In this work, we employed two indirect methods to obtain Henry's constants of CO₂ in pure MEA. One is the CO₂–N₂O analogy method, and the other is the plant-data-optimization method.

Table 2. Temperature Dependence of Henry's Constants for Carbon Dioxide

$$\ln H_{i-s} = C_1^H + C_2^H/T + C_3^H \ln T + C_4^H T$$

	C_1^H	C_2^H	C_3^H	C_4^H	ref
CO ₂ –H ₂ O	170.7126	-8477.711	-21.95743	0.005 780 748	<i>a</i>
CO ₂ –MEA	89.452	-2934.6	-11.592	0.016 44	<i>b</i>

^a Austgen et al.¹ ^b Equation 10 using data from Austgen et al.,¹ Wilhelm et al.,¹⁷ and Wang et al.¹⁶

**Figure 1.** Temperature dependence of Henry's constants of CO₂ in water and in MEA.

The CO₂–N₂O analogy method is based on the proposal by Clarke¹⁵ that if CO₂ reacts with a solvent, its true solubility can be determined by the proportionality to the solubility of a similar gas that is unreactive to the solvent. N₂O is usually used as the similar gas for CO₂ with regard to pure alkanolamines because it has molecular weight, configuration, volume, electronic structure, and Lennard-Jones potential very similar to those of CO₂ and it is unreactive to alkanolamines. The CO₂–N₂O analogy method in the Henry's constant form is expressed as

$$H_{\text{CO}_2\text{--MEA}} = H_{\text{CO}_2\text{--H}_2\text{O}} \frac{H_{\text{N}_2\text{O--MEA}}}{H_{\text{N}_2\text{O--H}_2\text{O}}} \quad (10)$$

In this work, the temperature dependence of Henry's constants has the same functional form as that of eq 9. The units are Pascals. Table 2 gives the coefficients of Henry's constants of CO₂ in water and in MEA. The former is just the same as that in the work by Austgen et al.¹ The latter is obtained using eq 10, where the required Henry's constant for N₂O in MEA is from Wang et al.¹⁶ and that for N₂O in water is from Wilhelm et al.¹⁷ Figure 1 shows the temperature dependency of Henry's constants of CO₂ in water and in MEA. Noted that the two Henry's constant lines intersect at about 3.8 °C (276.95 K), which is much lower than the intersecting point of 40 °C for CO₂ in water and in MDEA reported by Posey.¹⁸

To verify Henry's constant of CO₂ in MEA obtained using eq 10, we designed a plant-data-optimization method to obtain Henry's constant of CO₂ in MEA independently. In essence, Henry's constant of CO₂ in MEA was treated as an adjustable parameter to optimize the results of three industrial cases for CO₂ removal. It was a surprise to find that Henry's constants

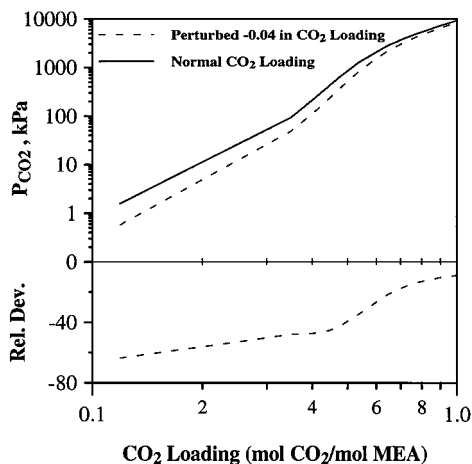


Figure 2. Partial pressure and relative deviation of CO₂ in a MEA (30 wt %)-H₂O system at 120 °C with normal CO₂ loading as well as those perturbed -0.04. The model with the fitted parameter from this work was used in the calculation. The relative deviation is calculated by $(P_{\text{ptb}} - P_{\text{normal}})/P_{\text{normal}} \%$.

of CO₂ in MEA obtained from the two independent methods match so closely with each other. The relative differences are smaller than 0.8%. The verification indicates that Henry's constants of CO₂ in MEA obtained from eq 10 can be used with confidence.

Evaluation of Experimental Data. Because MEA is one of the first alkanolamines commercially used for treating acid gas and is still widely used, a large amount of experimental VLE data for the MEA-CO₂-H₂O system have been published. A detailed list for the most published papers presenting the experimental data on the subject can be found in the book by Kohl and Nielsen.¹³

Austgen and co-workers used experimental VLE data of the MEA-CO₂-H₂O system from five different sources in the data regression to determine the adjustable parameters of the model. The five data sources are Lee et al.,¹⁹ Isaacs et al.,²⁰ Lawson and Garst,²¹ Jones et al.,²² and Muhlbauer and Monaghan.²³ There is significant inconsistency of the experimental data among the five sources. Because of lack of the information regarding the data quality of these sources, Austgen and co-workers thought that the best approach was to treat the five data sources equally with a weighting factor of 1 for each of them.

In this work, we studied the quality of the experimental VLE data for the MEA-CO₂-H₂O system. We found that a key factor that is critical to the data quality is the accuracy of the measured CO₂ concentration in the liquid phase. In the normal CO₂ loading (moles of CO₂ per moles of MEA) range, the partial pressure of CO₂ arises so fast that it spans about 8 orders of magnitude. Therefore, any small measurement error of the CO₂ concentration will cause a large deviation in the partial pressure of CO₂. For example, Jou et al.²⁴ pointed out that there was a systematic error of about -0.04 mol of CO₂/mol of MEA in the VLE measurement for the MEA-CO₂-H₂O system by Lee et al.²⁵ The upper part in Figure 2 shows a partial pressure of CO₂ in a MEA (30 wt %)-H₂O system at 120 °C with normal CO₂ loading as well as with the CO₂ loading shifted -0.04. The model with a fitted parameter from this work was used in the calculation. Suppose the calculated partial pressure of CO₂ corresponding to the normal CO₂ loading is correct and is used as the

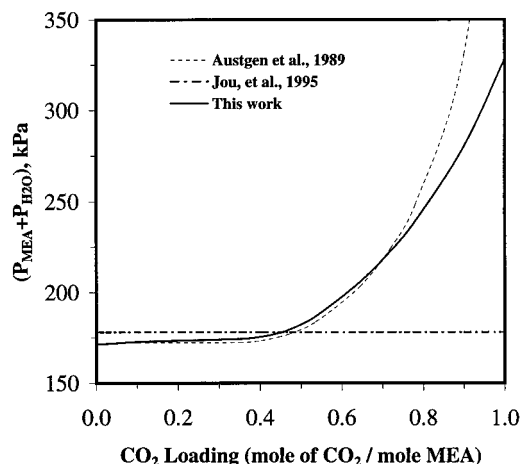


Figure 3. Comparison of the sum of partial pressures for MEA and H₂O in a MEA (30 wt %)-H₂O system with the CO₂ loading from 0 to 1 at the temperature of 120 °C.

standard for comparison, the lower part in Figure 2 illustrates that an error of -0.04 CO₂ loading can produce around and beyond 40% deviation on the partial pressure of CO₂. We also found one factor that may be overlooked when measuring the VLE data for the MEA-CO₂-H₂O system. Using a common static apparatus to measure the solubility of CO₂ in a MEA-H₂O system, Jou et al.²⁴ used Raoult's law to calculate the sum of partial pressures for MEA and H₂O and then subtracted the value from the total pressure to obtain the sum of partial pressures for CO₂ and an inert gas, which was added to maintain the apparatus pressure. The nonideality in the MEA-H₂O system was neglected and so was the effect of the dissolved CO₂ on the partial pressures of MEA and water. These negligences might cause noticeable errors in the final results, especially in the high-temperature region. Figure 3 shows a comparison of the sum of partial pressures for MEA and H₂O in a MEA (30 wt %)-H₂O system with a CO₂ loading from 0 to 1 at the temperature of 120 °C using three different models. The dashed line was calculated using the model of Austgen et al.¹ The dot-dashed line was obtained based on Raoult's law, which was used by Jou et al.²⁴ to deduce the partial pressure of CO₂ from the raw measuring data. The solid line was calculated using the model with a fitted parameter from this work. It is clear that over 0.5 CO₂ loading the nonideality of the MEA-H₂O system as well as the effect of the dissolved CO₂ should not be neglected. What we found explains, in part, why there is significant inconsistency of the experimental VLE data for the MEA-CO₂-H₂O system among various sources. A quality evaluation of the various data sources is highly necessary. The accurate and reliable VLE measurement on the MEA-CO₂-H₂O system still remains as one of the most challenging tasks for the chemical engineering experimentalists.

In this work, we followed the work of Weiland and co-workers⁷ in a quality evaluation of the various data sources. The electrolyte NRTL model was used to do a preliminary two-stage fit of the VLE data for the MEA-CO₂-H₂O system from six sources: five used by Austgen et al.¹ and one from Jou et al.²⁴ The fitting error of each data source was analyzed, and the data sources that appeared to deviate significantly were excluded in the final data regression. The excluded data sources were those from Isaacs et al.,²⁰ Jones et al.,²² and

Table 3. Fitted Interaction Parameter Values for the MEA-CO₂-H₂O and CO₂-H₂O Systems Using the Electrolyte NRTL Model^a

a. MEA-CO ₂ -H ₂ O System			
molecule-molecule parameter	$A_{mm'}$	$B_{mm'}$	ref
MEA-H ₂ O	-1.609 693	-265.1962	<i>b</i>
H ₂ O-MEA	1.648 945	125.0832	<i>b</i>
molecule-ion pair (ion pair-molecule) parameter	$\tau_{m,ca}(\tau_{ca,m})$		
H ₂ O-(MEA ⁺ , HCO ₃ ⁻)	0.129 079 6		<i>c</i>
(MEA ⁺ , HCO ₃ ⁻)-H ₂ O	-0.424 708 7		<i>c</i>
H ₂ O-(MEA ⁺ , MEACOO ⁻)	4.352 250		<i>c</i>
(MEA ⁺ , MEACOO ⁻)-H ₂ O	-3.340 842		<i>c</i>
b. CO ₂ -H ₂ O System ^d			
molecule-molecule parameter	$A_{mm'}$	$B_{mm'}$	$\alpha_{mm'}$
CO ₂ -H ₂ O	10.064	-3268.135	0.20
H ₂ O-CO ₂	10.064	-3268.135	0.20
molecule-ion pair (ion pair-molecule) parameter	$\tau_{m,ca}(\tau_{ca,m})$	$\alpha_{m,ca}(\alpha_{ca,m})$	
H ₂ O-(H ₃ O ⁺ , HCO ₃ ⁻)	8.0	0.2	
(H ₃ O ⁺ , HCO ₃ ⁻)-H ₂ O	-4.0	0.2	
H ₂ O-(H ₃ O ⁺ , OH ⁻)	8.0	0.2	
(H ₃ O ⁺ , OH ⁻)-H ₂ O	-4.0	0.2	
H ₂ O-(H ₃ O ⁺ , CO ₃ ²⁻)	8.0	0.2	
(H ₃ O ⁺ , CO ₃ ²⁻)-H ₂ O	-4.0	0.2	
CO ₂ -(H ₃ O ⁺ , HCO ₃ ⁻)	15.0	0.1	
(H ₃ O ⁺ , HCO ₃ ⁻)-CO ₂	-8.0	0.1	
CO ₂ -(H ₃ O ⁺ , OH ⁻)	15.0	0.1	
(H ₃ O ⁺ , OH ⁻)-CO ₂	-8.0	0.1	
CO ₂ -(H ₃ O ⁺ , CO ₃ ²⁻)	15.0	0.1	
(H ₃ O ⁺ , CO ₃ ²⁻)-CO ₂	-8.0	0.1	

^a NRTL nonrandomness factors for these fitted parameters were fixed at 0.2 except CO₂-ion pair (ion pair-CO₂) parameters.

^b Nath and Bender,²⁷ Touhara et al.,²⁸ and Kohl and Nielsen.¹³

^c Lee et al.,¹⁹ Lawson and Garst,²¹ and Jou et al.²⁴ ^d The parameter values were obtained from Austgen et al.¹

Muhlbauer and Monaghan,²³ Weiland and co-workers⁷ also observed that these three data sources were less accurate. For the data source of Jou et al.,²⁴ we eliminated the data points over 0.5 CO₂ loading for the reason mentioned in the above paragraph.

Equilibrium Constant and Interaction Parameters from Data Regression. Equilibrium constant of carbamate reversion reaction (reaction 6e) and some of the interaction parameters of the electrolyte NRTL model were obtained from the regression of the relevant experimental data.

In the MEA-CO₂-H₂O system, there are three molecular species and six ionic species created by reactions 6a-e. The corresponding interaction parameters in the electrolyte NRTL model will be 6 molecule-molecule, 24 molecule-ion pair (ion pair-molecule), and 54 ion pair-ion pair. Because about half of the species are present in the liquid phase at a low or negligible amount, the parameters associated with them do not significantly affect the VLE representation for the system. In this work, only the interaction parameters that significantly affect the VLE representation were fitted to the experimental data. They are listed in Table 3a. Table 3b shows the interaction parameters related to the binary CO₂-H₂O system. The values of those parameters were obtained directly from the work of Austgen et al.¹ All other parameters not reported in

Table 3a,b were regarded as unimportant, which include two molecule-molecule, most of the molecule-ion pair (ion pair-molecule), and all of the ion pair-ion pair interaction parameters. These unimportant parameters were assigned a default value of zero. From the theoretical point of view, the default value of zero essentially reduces the electrolyte NRTL model to the Pitzer-Debye-Hückel equation for the relevant ionic species with an insignificant amount and to Raoult's law for the relevant molecular species. Note that there is a difference in the parameter defaulting (except the parameters listed in Table 3b) between this work and the work by Austgen et al.¹ Austgen and co-workers used 8 and -4 as default values for the water-ion pair and ion pair-water interaction parameters, respectively. They used 15 and -8 as default values for MEA-ion pair and ion pair-MEA as well as CO₂-ion pair and ion pair-CO₂ interaction parameters, respectively.

In this work, the temperature dependence of the molecule-molecule interaction parameters is given as

$$\tau_{mm'} = A_{mm'} + B_{mm'}/T \quad (11)$$

The molecule-ion pair (ion pair-molecule) interaction parameters are assumed to be temperature independent. The NRTL nonrandomness factor is fixed at 0.2 for molecule-molecule, water-ion pair, and ion pair-water interaction parameters.

Data regression for determining the parameter values was carried out using an algorithm derived by Britt and Luecke.²⁶ The objective function is formulated based on the maximum likelihood principle and is given as

$$F = \sum_l \sum_{l'} \frac{N_D N_V}{\sigma} \left[\frac{(Z^{\text{cal}} - Z^{\text{exp}})^2}{\sigma} \right]_{l,l'} \quad (12)$$

where the summation is over all of the measured variables, N_V , for all of the data points, N_D . Z^{cal} and Z^{exp} are calculated and experimental values, respectively. σ is the standard deviation of measurement for the l th data point of the l' th measured variable. To make the comparison easier between the data regression results from the work of Austgen et al.¹ and those from this work, we used the same standard deviation values assigned by Austgen et al.¹

The MEA-H₂O and H₂O-MEA interaction parameters were fitted based on the experimental data for the MEA-H₂O system. The experimental data used by Austgen et al.¹ were the VLE data only. Posey¹⁸ used the VLE data, the heat-mixing data, and the freezing-point data altogether for the fitting and obtained more reliable parameter values. In this work, the VLE data, the heat-mixing data, the heat capacity data, and the pH data were fitted simultaneously and the fitted values of the MEA-H₂O and H₂O-MEA interaction parameters are given in Table 3a.

In the work of Austgen et al.,¹ the equilibrium constant of the carbamate reversion reaction (reaction 6e) and the four important water-ion pair (ion pair-water) interaction parameters of the electrolyte NRTL model were simultaneously fitted based on the VLE data for the MEA-CO₂-H₂O system. As discussed in the section Equilibrium Constants for the Reactions in the Liquid Phase, we adopted the two-stage procedure proposed by Weiland et al.⁷ in the data regression. In the first stage, the equilibrium constant of reaction 6e was fitted with the values of the four important water-

Table 4. Comparison between the Model of Austgen et al.¹ and Its Improved Version of This Work on the Root-Mean-Square Relative Deviation of Partial Pressure for CO₂, σ_{P,CO_2} , as Well as That of the Liquid-Phase Mole Fraction for CO₂, σ_{x,CO_2} , at the Temperature Range of 25–120 °C and the MEA Concentration Range of 1.0–5.0 M^a

temp, °C	MEA concn 1.0 M		MEA concn 2.5 M		MEA concn 3.75 M		MEA concn 5.0 M	
	σ_{P,CO_2}	σ_{x,CO_2}	σ_{P,CO_2}	σ_{x,CO_2}	σ_{P,CO_2}	σ_{x,CO_2}	σ_{P,CO_2}	σ_{x,CO_2}
This Work								
25	0.0545	0.0616	0.0178	0.0280	0.0071	0.0197	0.0163	0.0260
40	0.0546	0.0762	0.1020	0.0489	0.0189	0.0384	0.0113	0.0223
60	0.0314	0.0477	0.0139	0.0237	0.0082	0.0145	0.0088	0.0154
80	0.0551	0.0642	0.0355	0.0306	0.0318	0.0293	0.0354	0.0403
100	0.0886	0.0482	0.0422	0.0318	0.0160	0.0191	0.0257	0.0379
120	0.0531	0.0427	0.0964	0.0728	0.1050	0.0839	0.1130	0.0987
average	0.0588	0.0584	0.0610	0.0415	0.0429	0.0394	0.0468	0.0463
Austgen et al.								
25	0.0407	0.0768	0.0255	0.0641	0.0283	0.0694	0.0312	0.0661
40	0.0677	0.1080	0.1730	0.1100	0.0688	0.1217	0.0645	0.1120
60	0.0586	0.0821	0.0642	0.0858	0.0668	0.0889	0.0561	0.0778
80	0.0692	0.0720	0.0642	0.0740	0.0660	0.0704	0.0764	0.0686
100	0.1070	0.0699	0.1170	0.0874	0.1260	0.0842	0.1490	0.0920
120	0.0977	0.0833	0.1220	0.1020	0.1160	0.1040	0.0975	0.1020
average	0.0762	0.0831	0.1050	0.0882	0.0842	0.0912	0.0871	0.0875

^a The results were based on the experimental data from Lee et al.¹⁹

ion pair (ion pair–water) interaction parameters defaulted to zero. In the second stage, the values of the equilibrium constant for reaction 6e obtained in the first stage were kept unchanged and the four relevant interaction parameters were fitted to achieve the best possible results. In both stages, the same VLE data for the MEA–CO₂–H₂O system were used. The fitted values from the first stage can be found in Table 1 and those from the second stage in Table 3a. Because both water and MEA were treated as solvents, when proper MEA–H₂O and H₂O–MEA interaction parameters were provided, a theoretically more sound way to obtain the values of the equilibrium constant for reaction 6e is to use only the low loading VLE data in the first-stage fitting, and then in the second stage the four relevant interaction parameters are fitted based on the VLE data of the whole loading range. However, when the model with parameter values fitted using this approach was applied to simulate three industrial cases for CO₂ removal, the results showed a general trend that the reboiler heat duties were somewhat underpredicted. We think that it might be caused by the poor accuracy of the low loading VLE data for the MEA–CO₂–H₂O system.

Table 4 gives a comparison between the model of Austgen et al.¹ and its improved version of this work on the root-mean-square relative deviation of the partial pressure for CO₂ as well as that of the liquid-phase mole fraction for CO₂ at the temperature range of 25–120 °C and the MEA concentration range of 1.0–5.0 M. The comparison is based on the result from fitting the VLE data of Lee et al.,¹⁹ which is the main data source in this work. It is apparent that the root-mean-square relative deviations from this work are smaller than those from Austgen et al.¹ at all of the temperature and concentration ranges. The main reason for that is that we used fewer but more consistent data sources in the data regression.

Parts a and b of Figure 4 are the speciation–concentration plots which show how the concentration of each key species varies with the CO₂ loading from 0 to 1 in a 2.5 M MEA solution at temperatures of 40 and 120 °C, respectively. The speciation and concentration of each key species were predicted using the liquid-phase reactions of 6a–e as well as the electrolyte NRTL model with the parameter values fitted in this work.

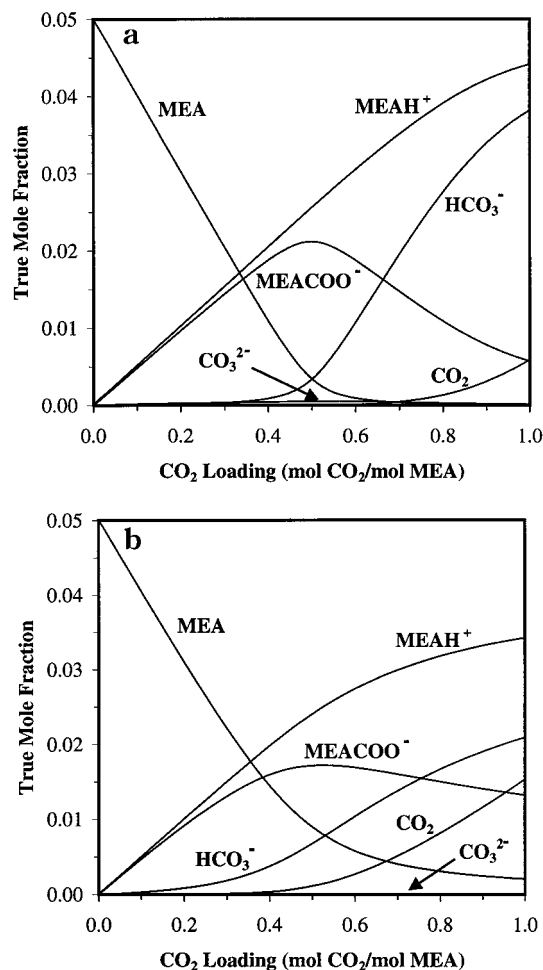


Figure 4. Liquid-phase speciation and concentration in a 2.5 M MEA solution with CO₂ loadings from 0 to 1 at temperatures of (a) 40 and (b) 120 °C. The speciation and concentration were predicted using the liquid-phase reactions of 6a–e as well as the electrolyte NRTL model with the parameter values fitted in this work.

Note that the speciation–concentration plots from this work are very similar to the corresponding speciation–concentration plots from the work by Austgen et al.¹ The speciation–concentration plot is a useful tool in analyzing simulation results of the aqueous MEA absorber

Table 5. Comparison against Plant Data between the Model of Austgen et al.¹ and This Work on the Simulation of Three Industrial Cases for CO₂ Removal Using the Aqueous MEA Absorption/Stripping Processes^a

	case 1		case 2		case 3	
	Austgen et al.	this work	Austgen et al.	this work	Austgen et al.	this work
Absorber						
gas inlet temp, F	0.00	0.00	0.00	0.00	0.00	0.00
gas inlet pressure, psi	0.00	0.00	0.00	0.00	0.00	0.00
gas outlet temp, F	0.02	0.02	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
gas outlet pressure, psi	-0.46	-0.46	0.00	0.00	-0.02	-0.02
gas outlet CO ₂ , ppmv	211.11	0.00	206.67	26.67	-70.37	-14.81
lean inlet temp, F	0.02	0.02	0.48	0.48	0.03	0.03
rich outlet temp, F	-3.76	-3.43	<i>b</i>	<i>b</i>	0.58	-0.51
Stripper						
rich inlet temp, F	0.25	0.11	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
lean outlet temp, F	<i>b</i>	<i>b</i>	-0.16	0.12	0.07	0.26
lean outlet pressure, psi	<i>b</i>	<i>b</i>	0.00	0.00	0.00	0.00
reboiler duty, mmbtu/h	58.43	8.99	13.73	-5.49	35.11	4.58
condenser temp, F	0.00	0.00	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
loading, mol/mol						
lean solution	0.00	0.00	0.00	0.00	0.00	0.00
rich solution	-9.85 ^c	-9.85 ^c	<i>b</i>	<i>b</i>	0.00	0.00

^a The results are in percent and expressed as $(Z^{\text{pred}} - Z^{\text{plant}})/Z^{\text{plant}}\%$. ^b Plant data are not available. ^c Plant data does not satisfy mass balance.

column for CO₂ removal using mass- and heat-transfer rate-based simulation models.

Process Simulation

The ultimate test of the capability and accuracy of the model improved in this work was to apply it in the simulation of the aqueous MEA absorption/stripping processes for CO₂ removal. The availability of the operating data of the process, obtained under stable conditions, as well as the relevant equipment data was indispensable for such simulations. Although the complete and consistent sets of the operating and equipment data for the industrial processes using aqueous MEA for CO₂ removal were not so easy to find, we had the opportunity to obtain the plant data for three industrial cases.

All three cases used the basic process flow scheme in conventional alkanolamine acid-gas absorption/stripping processes. Gas to be purified is passed upward through the absorber column, countercurrent to the CO₂-lean aqueous MEA solution. The CO₂-rich aqueous MEA solution from the bottom of the absorber column is heated by the heat exchange with the CO₂-lean aqueous MEA solution from the bottom of the stripping column and is then fed to the stripping column at some point near the top. After CO₂ is stripped, the CO₂-lean aqueous MEA solution from the bottom of the stripping column is first partially cooled in the lean-to-rich solution exchanger and is then further cooled by heat exchange with water or air and thereafter is fed to the top of the absorber column to complete the cycle. Despite the fact that all three cases use a similar process flow scheme, the operating conditions and equipment data of the three cases vary widely. The absorber pressure ranges from about 180 to 950 psi. The lean CO₂ loading (mole of CO₂ per mole of MEA) ranges from about 0.1 to 0.2 and the rich CO₂ loading from about 0.3 to 0.55. The MEA concentration ranges from about 20 to 30 wt %. The column type can be tray column or packed column, and the column diameter ranges from about 1 to 2 m.

The rate-based approach (RATEFRAC) in Aspen Plus process simulator was used to simulate the aqueous MEA absorber column for CO₂ removal. This approach

considers (1) material and energy balance, (2) mass and energy transfer rate, (3) vapor-liquid equilibrium, and (4) liquid-phase reactions and reaction rate on each actual tray (or section of packing). Generally speaking, this approach describes what actually occurs on a tray (or section of packing) rather than the phase equilibrium that does not exist anywhere in the column. Therefore, the concept of the tray (or section of packing) efficiency is avoided entirely. It is worth mentioning that the state-of-the-art rate-based approach with accurate thermodynamic and transport property models is a very useful tool to develop and operate more energy-efficient alkanolamine acid-gas absorption/stripping processes and to achieve competitive edges in the sophisticated column design, especially in the design of the acid-gas selective absorption where too many trays (or sections of packing) can destroy the selectivity while too few can cause outlet gas off specification.

For simulation of the stripping column, the traditional phase-equilibrium approach is applied. According to the discussion on stripping by Kohl and Riesenfeld,²⁹ we specified about 10 theoretical trays below the CO₂-rich solution feeding point as the stripping section of the column and two theoretical trays above the point as the MEA recovering section.

Table 5 shows the simulation results for the three industrial cases using the model improved in this work. For comparison, the model of Austgen et al.¹ was also applied to simulate the three industrial cases, and the results are included in Table 5. Both simulation results were expressed as

$$\frac{(Z^{\text{pred}} - Z^{\text{plant}})}{Z^{\text{plant}}}\%$$

where Z^{pred} is the predicted values and Z^{plant} is the corresponding plant data. In case 1, the reaction rate (kinetics) provided by the Aspen Plus process simulator was applied without modification in the absorber simulation using the rate-based approach, and the simulation result was very satisfactory. However, when we applied the same reaction rate in case 2, we found that some modification on the reaction rate was necessary. Note that the reaction rate is one of the key issues for

a successful simulation of alkanolamine acid–gas absorption/stripping processes using the rate-based approach and currently is an active research area. We intend to discuss this topic in a subsequent paper. In case 3, because of the lack of equipment data, the absorber column was simulated using the traditional phase-equilibrium approach with proper consideration of tray efficiencies. From Table 5, one can see without a doubt that the model improved in this work gives better simulation results upon the three industrial cases than the model by Austgen et al. The reboiler heat duties predicted by the model improved in this work were within the uncertainties of the plant data for all three industrial cases.

Conclusion

In comparison to the work of Austgen et al.,¹ the electrolyte NRTL model has been applied in a thermodynamically consistent manner to provide a better representation of the vapor–liquid equilibrium (VLE) for the aqueous MEA–CO₂ system. Rigorous chemical equilibria in the liquid phase have been considered. It has been found that the accurate VLE description of the system at a temperature of around 120 °C is critical to a successful simulation of the stripper column of the aqueous MEA absorption/stripping processes for CO₂ removal. The influence from chemical equilibrium constants, Henry's constant, experimental data, and data regression on the VLE of the system has been discussed in detail. The equilibrium constant of the carbamate reversion reaction as well as important interaction parameters of the electrolyte NRTL model have been fitted to experimental data using a two-stage procedure, and good agreement between the calculated values and the experimental data has been achieved. The model with newly fitted parameters has been successfully applied to simulate three industrial cases for CO₂ removal using the rate-based approach. For comparison, the model of Austgen et al.¹ has also been applied to simulate the same cases. The simulation results are in favor of the model from this work. Currently, efforts are being made on the accurate VLE representation for the aqueous DEA acid–gas system, the aqueous MDEA acid–gas system, and the mixed alkanolamine acid–gas systems.

Acknowledgment

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Nomenclature

A, B = constants in eq 11
 C = temperature coefficient
 D = dielectric constant
 F = objective function
 H = Henry's constant
 K = equilibrium constant
 M = molarity
 M_s = solvent molecular weight
 N_0 = Avogadro's number
 P = pressure
 P_m^0 = saturation pressure of the solvent mixture

P_s^0 = saturation pressure of solvent s
 R = gas constant
 T = temperature, K
 X = effective mole fraction
 Z = absolute value of the ionic charge
 Z^{cal} = calculated value in eq 12
 Z^{exp} = experimental value in eq 12
 Z^{pred} = predicted value in simulation
 Z^{plant} = plant data
 e = electron charge
 d = solvent density
 g = Gibbs energy
 k = Boltzmann constant
 n_t = total mole number for all species in the system
 n_i = mole number of species i
 r = Born radius
 v = molar volume
 $\bar{v}$ = partial molar volume
 w_s = weight fraction
 x = true liquid-phase mole fraction based on all species: molecular and ionic
 y = vapor-phase mole fraction

Greek Letters

α = NRTL nonrandomness factor
 γ = activity coefficient
 ρ = closest approach parameter of the Pitzer–Debye–Hückel equation
 σ = measured standard deviation in eq 12 or root-mean-squares relative deviation in Table 4
 τ = NRTL interaction parameter
 ϕ^0 = pure solvent vapor-phase fugacity coefficient at saturation pressure
 ϕ^v = vapor-phase fugacity coefficient

Superscripts

$*$ = unsymmetrical convention
 ∞ = infinite dilution
 Born = Born contribution
 ex = excess property
 H = Henry's constant
 k = equilibrium constant
 lc = local-composition NRTL equation
 n_D = number of data points
 n_V = number of measured variables
 0 = saturation
 PDH = Pitzer–Debye–Hückel equation
 w = water

Subscripts

a, a', a'' = anion
 c, c', c'' = cation
 i, j, k = any species
 i–m = solute i in solvent mixture
 i–s = solute i in solvent s
 l = l th data point
 l' = l' th measured variable
 m, m' = molecular species
 P = pressure
 s = solvent
 w = water
 x = true mole fraction

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